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TITLE: Forming shaped porous plastic articles having uniform porosity - by working the plastic to heat it to a rubber-like state, forcing through orifices to form discrete particles and then through a shaping die

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WO 9205946 A	April 16, 1992	E	027	N/A
DE 69132455 E	November 30, 2000	N/A	000	B29C
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AU 9185433 A	April 28, 1992	N/A	000	B29C
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EP 551335 A1	July 21, 1993	E	027	B29C
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WO 9205946A	N/A	1991WO-GB01671	September 27, 1991
DE 69132455E	N/A	1991DE-0632455	September 27, 1991
DE 69132455E	N/A	1991EP-0917226	September 27, 1991
DE 69132455E	N/A	1991WO-GB01671	September 27, 1991
DE 69132455E	Based on	EP 551335	N/A
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AU 9185433A	N/A	1991WO-GB01671	September 27, 1991
AU 9185433A	Based on	WO 9205946	N/A
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EP 551335B1	N/A	1991EP-0917226	September 27, 1991
EP 551335B1	N/A	1991WO-GB01671	September 27, 1991
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USE/ADVANTAGE - The porous article may be a pipe, rod or sheet and may be for use as a filter for air, water, fuel or blood serum, or in aquarium aerators, breather vents, dessicant holders, metering devices, marker tips, fragrance reservoirs, foaming devices, pneumatic mufflers, oxygen humidifiers, or battery flame arrestors. The method insures uniform heating of the material and uniform porosity in the article

ABSTRACTED-PUB-NO: WO 9205946A

EQUIVALENT-ABSTRACTS:

USE/ADVANTAGE - The porous article may be a pipe, rod or sheet and may be for use as a filter for air, water, fuel or blood serum, or in aquarium aerators, breather vents, dessicant holders, metering devices, marker tips, fragrance reservoirs, foaming devices, pneumatic mufflers, oxygen humidifiers, or battery flame arrestors. The method insures uniform heating of the material and uniform porosity in the article

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<p>(21) International Application Number: PCT/GB91/01671 (22) International Filing Date: 27 September 1991 (27.09.91) (30) Priority data: 9021344.8 1 October 1990 (01.10.90) GB (71) Applicant (for all designated States except US): EVANS, David, Charles [GB/GB]; More Place, Wonham Lane, Betchworth, Surrey RH3 7AD (GB). (71)(72) Applicant and Inventor: ENGEL, Thomas, Paul [DE/FR]; "La Pastorale", 302, chemin de la Billoire, F-06140 Vence (FR). (74) Common Representatives: EVANS, David, Charles et al.; F.J. Cleveland & Company, 40/43 Chancery Lane, London WC2A 1JQ (GB).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), SU⁺, US. Published With international search report.</p>
<p>(54) Title: PRODUCTION OF POROUS PLASTIC MATERIALS</p>		
<p>(57) Abstract</p> <p>The present invention relates to a method of forming a shaped porous article (20) formed of a plastics material characterised in that the method comprises working said plastics material to increase the temperature thereof to a level at which the material exhibits a rubber-like consistency, and forcing the conditioned material through orifice means to cause or allow the material to form discrete particles and thereafter passing said particles through shaping means (13) to cause or allow said particles to adhere one to another to form a shaped porous article (20) of said plastics material.</p>		

+ DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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PRODUCTION OF POROUS PLASTIC MATERIALSDESCRIPTION

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This invention relates to the production of porous plastic materials and to shaped articles made therefrom. Porous plastic components are well known and have been used for many years. Hitherto, production of such

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material has been carried out by sintering granules or particles of plastics materials in a mould. In order to achieve uniform properties for such a material it is necessary to achieve uniform conditions of sintering throughout the plastics material during the formation of

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the shaped porous product. In order to achieve sintering temperature, it is necessary to apply heat to the plastics material; since plastics materials are generally poor conductors of heat, this results in a non-uniform temperature distribution during the sintering step.

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Furthermore, the use of such sintered materials in high temperature environments has been restricted simply because sintering requires melting or softening of

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surface lamina of the particles of plastics materials in order to induce fusion at their contact point.

5 High temperature materials and high strength materials have become available, but methods of production are complex and the materials are necessarily expensive. Porous materials are currently available from a variety of manufacturers formed of nylon 6, polysulfone, polycarbonate polyphthalate carbonate and
10 polytetrafluoroethylene among others.

Porous and microporous plastics materials are much employed for filters and separators and used in the fluidisation of liquids, solids and gases. The usual
15 function of these porous plastic materials is to filter liquids such as water, oil, fuel and chemicals, to purify air, or to separate out components such as dust, asbestos, silicas and heavy metals. Such porous materials find application in the fluidisation of bulk
20 solids for conveying and storing, and also in industrial vacuum cleaning and filtration equipment.

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All current methods of producing porous materials rely as an essential step on the presence of a substance which either is gaseous or is capable of becoming gaseous under the processing conditions, such substance being e.g. a
5 gas, chemical blowing agent, or volatile solvent.

As stated above, one of the difficulties of current methods of production of porous plastics materials is the uniformity of porous properties throughout the material.
10 In some uses, such for example, as shoe insoles and dust filters in vacuum cleaners, this is not a problem, but in processes where careful control of particle size or rates of passage of materials through a separator are of importance such as in medical filters, controlled rate
15 release devices and pen nibs, then such control of the particle size becomes of increasing importance. In view of the difficulty of controlling particle or pore size using blowing agents and the like, there is a need for a continuous process for the production of a porous
20 material in which porosity of the material can be controlled without reliance upon blowing agents.

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According to one aspect of the present invention,
therefore, there is provided a method forming a shaped
porous article formed of a plastics material which method
comprises working said plastics material to increase the
5 temperature thereof to a level at which the material
exhibits a rubber-like consistency, and forcing said
conditioned material through orifice means to cause or
allow the material to form discrete particles and
thereafter passing said particles through shaping means
10 to cause or allow said particles to adhere one to another
to form a shaped porous article of said plastics
material.

In another aspect of the invention, the material is
15 maintained at said elevated temperature and under
pressure to condition the same. The working of the
material to increase its temperature may be accompanied
by heating thereof; the purpose of working the material
to increase the temperature is to ensure substantially
20 uniform heating throughout the material.

The working of the plastics material may be effected
initially in a compression chamber, and valve means may
be provided to control the maximum pressure to be

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effective within the chamber. A rapid temperature increase at the end of the working period is effected at least in part by the generation of shear forces within the material. Additional shear forces may be generated by passing the material through said orifice means. This ensures that all the material is at a substantially uniform temperature during the subsequent processing steps. Apparatus such as that described in British Patent Specification No. 1158011 and 1431101 is suitable for the working of the plastics material prior to passage through the orifice means.

Plastics materials which can be used in the process of this invention are those which exhibit a substantially rubber-like nature when heated to slightly below the glass transition temperature and which behave, to some extent, as a cross-linked material. The effect of the conditioning of the material is to maintain the material at its elevated temperature, but at a temperature below that at which it becomes a free flowing melt; thus providing uniformity of temperature distribution. Thus, on forcing the material through the orifice means, the shear stresses induced in the material produce a sudden rise in temperature which results in the material

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changing its state and effectively breaking up to a plurality of small particles which adhere one to another at their contact points and which can be subsequently be shaped in a die to form either a continuous shaped
5 article or are subsequently molded. The particles formed immediately after passing through the orifice means have just sufficient capacity to stick together, but do not flow to form a homogeneous melt. The result may be a shaped article such, as for example, a layer, pipe, rod
10 or sheet which is formed of cohered, discrete particles and having a distinct and substantially uniform porosity.

The invention has been found to be particularly successful with ultra-high molecular weight polyethylene.
15 This material, typically that commercially available under the trade name "HOSTALEN GUR", has good corrosion and chemical resistance and can, certainly in filter applications, provide significantly longer service. The material is supplied in the form of a powder and has a
20 bulk density as a powder of about 0.2 grams per cubic centimetre to 0.5 grams per cubic centimetre and then can be used in continuous service at temperatures from -250°C to +90°C.

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In a preferred aspect of the present invention, the molecular weight of the ultra high molecular weight polyethylene is within the range of 3-7 million. The ultra high molecular weight polyethylene may be heated to
5 a temperature above 136°C and maintained at that temperature within the range of 140-160°C at which temperature it may be forced through the orifice means at a pressure of 4-17 kilograms/cm².

10 The orifice means may be a breaker plate having a plurality of discrete orifices. It is clear that the porosity of the resultant material is dependant upon the size of the orifices within the orifice means. The orifice means may be a single plate or may be one or more
15 plates used in combination. Additionally, a combination of breaker plates and screens with an array of orifices may be employed.

In a particular aspect of the invention, both the level
20 and the uniformity of the porosity can be controlled. For fine particle size in a microporous product, an appropriate combination of plate and screen is used, for example, the particles may pass into a die which is designed to shape the extrudate; if the die is

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substantially parallel-sided, and at the melt temperature, the fractured polymer is subjected to comparatively little back pressure as it flows through the die. In this condition, the particles adhere, but
5 spaces are left between them, and a porous material is extruded from the die. If, however, the die is designed to offer significant compression of the flowing particles by presenting a path of reducing area, the particles will be more highly compressed, and a product of lower
10 porosity is produced.

Furthermore, additional control can be exercised by controlling the die temperature; a hotter die presents less back pressure and results in a more porous material.
15 Where a screen is employed in combination with a breaker plate, the screen may serve to control further the particle size, possibly by providing further orifices to oversize material. The screen may be provided either in front or behind the breaker plate, or both in front and
20 behind. Where a multiple breaker plate assembly is employed, a screen or screens may be disposed between individual breaker plates within the assembly. Typical screens are formed of steel mesh.

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The Applicant has found that the incorporation of a blowing agent such, for example, as azo-dicarbonamide (1,1-azobis-formamide) such as that commercially available under the trade name "NITROSAN" may assist in the maintenance of the porosity during the shaping or molding step. The reason for this is that as the particles adhere during the forming step, in order to obtain optimum porosity, it is desirable that the particles adhere where they touch without significant flattening. The inclusion of a blowing agent allows the formation of slight positive pressure within the interstices of the packed particle assemblage during the shaping step and serves to maintain sufficient openness of the interstices of the particles to improve porosity. The amount of blowing agent added can be determined largely by experimentation; the addition of too much results in a partially blown product. Amounts within the range of 0.1% to 5% by weight have been found to be satisfactory with amounts preferably within the range of 0.15 to 0.5% by weight.

A proportion of a solvent for the plastics material may be incorporated within the material either prior to or during the working of the material. This is thought to

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assist in the conditioning step and to assist the adherence of the particles after formation by passing through the orifice means. The presence of a solvent or oligomers of the plastics material may further assist
5 shaping and porosity of the material after it has passed the orifice means. The solvent may be any solvent suitable for the plastics materials employed; such solvents are well known in the art.

10 In a further aspect of the present invention, cross-linking agents may be included to fix the particulate structure of the materials so formed. Typical cross-linking agents for polyethylene are peroxides such, for example, as dicumyl peroxide but any known
15 cross-linking agent for the plastics material may be employed. The effect of the cross-linking agent is to produce cross-linking. The cross-linking agent selected and the conditioning temperature, should be such that no significant cross-linking takes place or is initiated
20 before the material passes through the orifice means. The plastics material, prior to being subjected to the method of the invention, may also include antioxidants such for example as α -tocopherol, and bisphenols such as those commercially available under the trade name "IRGANOX".

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It should be noted, however, that the use of blowing agents, solvents and cross-linking agents are optional ingredients only and assist in the tailoring of the porous properties of the end product.

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The invention also includes porous and microporous plastics materials and articles made therefrom when produced by the method of the invention. The temperature rise resulting from passing the material through the
10 breaker plate may be such as to initiate the cross-linking reaction so that significant cross-linking commences only after formation of the discrete particles, or after the shaping of the particles. The mechanism of the invention is not, at present, understood, but it is
15 thought very likely that while the polymer is maintained at said elevated temperature during conditioning, it is partly crystalline even though the temperature is about 190°C. On passing through the fine holes of the breaker plate the temperature rises rapidly and of course
20 the polymer is strongly compressed in these fine holes. As the polymer leaves the holes, it expands suddenly, thus forming distinct particles and becomes porous. In the presence of a blowing agent or solvent (Gas) this sudden expansion is amplified, thus increasing the

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porosity. It has been observed that if the orifices within the breaker plate are large enough, then the plastics material simply flows straight through. When the size of the orifice(s) is reduced, porosity increases.

5

The shaping of the material after passage through the orifice means can also affect the resultant shaped product. For example, the back pressure generated by the shaping die appears to affect the final product. The material leaving the orifice means may be in the form of filaments or fibres. If the die has a large opening the fibers flow straight through. As soon as the opening is reduced in size the die fills and out comes a continuous rod which is packed loosely like a non-woven fabric. If the die is conical then the compacting of the fibers is higher. What has been observed is that the fiber is porous by itself, and that the compacting of the fiber makes the product porous too.

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The invention has been found to work well with plastics materials that do not have a melt index; for example ultra high molecular weight polyethylene at 200°C has a rubber like consistency; it does not stick. Once such

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a material has passed the orifice means, it does not coalesce.

5 Following is a description by way of example only and with reference to the accompanying informal drawing of methods of carrying the invention into effect.

In the drawing:-

10 Figure 1 is a diagram of the apparatus for forming a microporous tube.

A compressor 10 has a structure generally along the lines described in British Patent Specification No. 1158011.

15 The extruder is provided with an outlet barrel 11 constituting a plastising or conditioning chamber, a breaker plate 12 which comprises a plate fitted across the end of barrel 11 and having a plurality of longitionally extending orifices set in an array
20 thereacross, a back-up screen 13 and a shaping dye 14.

EXAMPLE 1

Ultra high molecular weight polyethylene commercially available under the trade name "HOSTALEN GUR 412" is

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premixed with 1.75% of dicumyl peroxide cross-linking agent and 0.5% by weight of a solvent and is then introduced into the compression chamber and subjected to working by the machine in the manner described in U.K. Patent Specification No. 1158011 together with external heat to raise the temperature of the material uniformly to 136°C. The material is maintained at a temperature of 140 to 150°C in a substantially plastic rubber-like condition within the conditioning chamber and then is urged under pressure of 16 kilograms per square centimetre through the orifices of the breaker plate. After passage through the breaker plate, the material is then shaped in the die 14 and thereafter withdrawn as an extruded tube 20 therefrom.

15

EXAMPLE 2

In another example of the present invention, ultra high molecular weight polyethylene, commercially available under the trade name "HOSTALEN GUR 412" was mixed with 0.7% by weight of solvent and then processed as described above. The resultant porous material can be heat welded, solvent welded or glued to form composite structures, either in the form of shapes and laminates. Such materials permit the formation of fibres, and porous

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plastics laminates which have a variety of uses in industry.

EXAMPLE 3

5 Example 2 was repeated, but the solvent was omitted. As before, the resultant porous material could be heat welded, solvent welded or glued to form composite structures either in the form of shaped or laminates.

10 In each of the above examples, the resultant tube is microporous and allows the passage of gas and liquids while retaining particles upon its surface. The process can be operated as a substantially continuous process and the pipe or tube drawn off and after cooling rolled for
15 subsequent use or for sale.

EXAMPLE 4

Ultra high molecular weight polyethylene commercially available under the trade name LUPOLEN 300 (molecular
20 weight 6 million, particle size largely between 100 and 300 microns) was mixed with 0.5% by weight of ammonium carbonate and 0.5% by weight of a stearamide slip agent commercially available under the trade name SYNTEWAX. Use of slip agents in the processing of plastics is well

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established in the art. The mixture was processed in the manner described for the previous examples.

5 The resulting tube was a rigid porous material of comparatively high strength. The tube had a wall thickness of 6 mm and an external diameter of 60.4 mm. Its porosity can be varied by altering the back pressure generated by the shaping die, whereby air permeability values between about 200 and 600 m³, per sq. metre per
10 minute at a pressure difference of 20 psi (138 kN/sq. metre) can be obtained.

EXAMPLE 5

15 Example 5 was repeated using 1% by weight ammonium carbonate instead of 0.5% air permeabilities between about 400 and 900 m³ per sq. metre per minute were obtained.

20 The tubes so produced find applications in sewage aeration, monitoring and abstraction of methane gas in landfill sites, and in piezometry (water sampling in the ground).

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EXAMPLE 6

LUPOLEN 300 ultra high molecular weight polyethylene was processed as described in Example 4 above except that the only additive was a stearamide slip agent SYNTEWAX
5 present in an amount of 0.5% by weight.

The resulting rigid porous tube had a wall thickness of 6.5 mm and an external diameter of 35 mm. Among other applications, the tube can be used for the aeration of
10 liquid flux used for the cleaning of surfaces about to be soldered.

Depending on the back pressure generated by the shaping die, this product had an air permeability of up to about
15 360 m^3 per sq. metre per minute at a pressure difference of 20 psi (138 kN/sq. metre).

The tubes produced in the last three examples are too rigid to be conveniently rolled up and are therefore cut
20 to the desired length.

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Porous products in accordance with the invention and as described above may be used in applicators, air regulator filters, aquarium aerators, biomedical filters, breather vents, desiccant holders, controlled metering devices, marker tips, fragrance reservoirs, membrane support media, foaming devices, reagent filters, pneumatic mufflers, blood serum filters, industrial filters, water-conditioning filters, filtration support media, oxygen humidifiers, fuel filters, battery flame arrestors, ETO vents and chromatography frits.

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CLAIMS

1. A method of forming a shaped porous article
formed of a plastics material characterised in that the
5 method comprises working said plastics material to
increase the temperature thereof to a level at which the
material exhibits a rubber-like consistency, and forcing
the conditioned material through orifice means to cause
or allow the material to form discrete particles and
10 thereafter passing said particles through shaping means
to cause or allow said particles to adhere one to another
to form a shaped porous article of said plastics
material.
- 15 2. A method as claimed in claim 1 characterised in
that after increasing the temperature to a level at which
the material exhibits a rubber-like consistency, the
material is maintained at said elevated temperature and
under pressure to condition the same prior to passage
20 through the said orifice means.
3. A method as claimed in claim 1 or claim 2
characterised in that the working of the material to

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increase its temperature is accompanied by external heating thereof.

4. A method as claimed in any preceding claim
5 characterised in that the working of the material is performed in a compression chamber incorporating valve means to control the maximum pressure to be effective within the chamber.

10 5. A method as claimed in any preceding claim characterised in that shear forces are generated as the material passes said orifice means.

15 6. A method as claimed in any preceding claim characterised in that the plastics material is an ultra high molecular weight polyethylene.

20 7. A method as claimed in any preceding claim characterised in that the orifice means comprises a breaker plate having a plurality of discrete orifices.

8. A method as claimed in any one of claims 1 to 7 characterised in that the orifice means comprises a plurality of plates used in combination.

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9. A method as claimed in claim 7 or 8 characterised in that one or more screens may be employed in combination with said orifice means.

5 10. A method as claimed in any preceding claim characterised in that a proportion of blowing agent is incorporated in the plastics material.

10 11. A method as claimed in claim 10 characterised in that the blowing agent is present in an amount of 0.1% to 5.0% by weight.

15 12. A method as claimed in claim 11 characterised in that the proportion of blowing agent is within the range of 0.15 to 0.50% by weight.

20 13. A method as claimed in any preceding claim characterised in that a proportion of the solvent for the plastics material is incorporated in the material either prior to or during working of the material.

14. A method as claimed in any preceding claim characterised in that a proportion of cross-linking agent

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is incorporated within the plastics material to fix the particulate structure of the material so formed.

15. A method as claimed in claim 14 characterised in
5 that the plastics material is a polyethylene, the
cross-linking agent is a dicumyl peroxide.

16. A method as claimed in any preceding claim
characterised in that a proportion of anti-oxidant is
10 incorporated in the plastics material.

17. A material comprising porous and/or microporous
plastics materials produced by a method claimed in any
preceding claim.

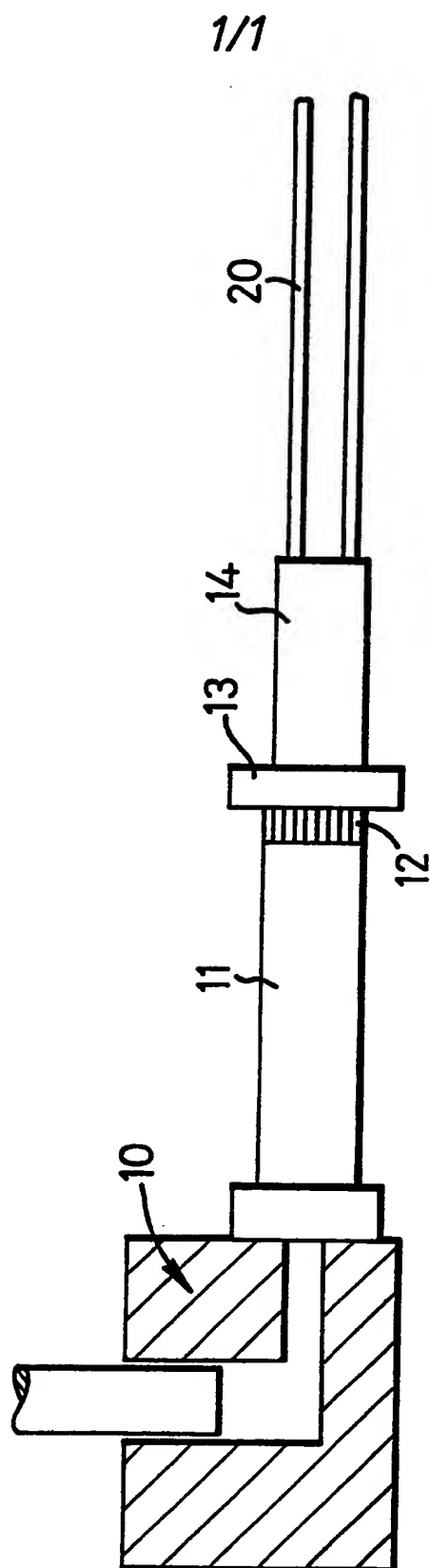


FIG. 1

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 375 441 (ADAMS ET AL.) 1 March 1983 see claims ---	1,2,17

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9101671
SA 51716

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/02/92. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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DE-A- 1729065	09-03-72	None	
US-A- 4375441	01-03-83	None	